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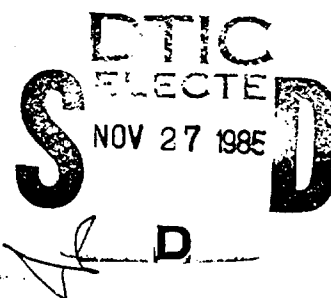
Cold Regions Research &
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Sample digestion and drying techniques for optimal recovery of mercury from soils and sediments

James H. Cragin and Brian T. Foley

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agreed within 20% of those for undried samples. Thus, any one of these three comparable methods is recommended for Hg determinations in soils and sediments. *Keywords:*

Chemical analysis; Volatilization.

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PREFACE

This report was prepared by James H. Cragin, Research Chemist, Snow and Ice Branch, Research Division, and Brian T. Foley, Physical Science Technician, Earth Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding for this project was provided by the U.S. Army Toxic and Hazardous Materials Agency. The authors thank Dr. J. Oliphant and T. Jenkins for technical review of the manuscript.

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SAMPLE DIGESTION AND DRYING TECHNIQUES FOR OPTIMAL RECOVERY OF MERCURY FROM SOILS AND SEDIMENTS

James H. Cragin and Brian T. Foley

INTRODUCTION

Determination of trace elements in soils and sediments usually involves sample drying, digestion and elemental analysis. The precision of the overall method is governed by the variability associated with each of these steps. The objective of this study was to assess the drying recovery and precision of analysis for a volatile metal, mercury, from various soils and sediments.

Since most common analytical techniques for mercury (atomic absorption spectrometry, flame emission spectrometry, inductively coupled plasma emission spectrometry and gold film mercury detection) require liquid samples for analysis, soils and sediments must first be digested. Before assessing sample drying effects, therefore, a simple, reliable and quantitative digestion technique must be selected. Historically, dissolution of rocks and minerals has been performed by fusion with Na_2CO_3 (Kolthoff and Sandell 1952) or by using HF in a pressure tight closed vessel (Bernas 1968). Both of these techniques are designed to dissolve refractory elements (Si, Al, Ti, Mn, Fe, Ca, Mg) composing the resistant aluminosilicate matrix.

Because of their greater surface area per unit weight, soils and sediments do not require such vigorous dissolution, especially for non-matrix pollutant elements such as Hg, Pb, Cd, Zn and As, which are generally sorbed on particle surfaces or complexed with organic matter. For this reason aqua regia is commonly used to dissolve soils, while oxidizing reagents (HNO_3 , HClO_4 , H_2SO_4 , H_2C_2) are used for sediments and soils containing appreciable amounts of organic matter. Oxidizing acids are especially important in the digestion of sediments for mercury in order to offset the reducing effect of organic carbon, which can result in loss

of mercury (as Hg^0) by volatilization (Knechtel and Frazer 1979). In fact, because of the strong potential for reduction-volatilization losses, any sample digestion for mercury should be conducted under oxidizing conditions. In this work, we present results of several digestion and drying techniques and the associated precision for select soil and sediment samples.

EXPERIMENTAL

Sample description

Two types of soils (Charlton silt and Windsor sand) and two sediments (Kewaunee sediment and LAAP pond sediment) were examined. Charlton silt is an uncontaminated silty loam from rural Hanover Center, N.H., while Windsor sand is an uncontaminated sandy loam from an area near Lebanon, N.H. An additional contaminated Windsor sand sample was taken from a CRREL test plot that had been irrigated with wastewater containing 1 mg Hg/L. Kewaunee sediment was grab-sampled from the harbor formed at the mouth of the Kewaunee River (Kewaunee, Wis.) and Lake Michigan. Because of its origin, this sample has been exposed to numerous industrial pollutants, including Hg. LAAP pond sediment was taken from Pond 9 of the Army ammunition plant at Dayline, Louisiana. This man-made settling pond was used for a number of years to dispose of spent dilute solutions of explosives as well as heavy metals.

Further description of the physical and chemical characteristics of these samples is given by Iskandar et al. (1976) for the Charlton and Windsor soils, by Iskandar et al. (1984) for the Kewaunee sediment and by Cragin et al. (1983) for the Louisiana sediment.

Drying techniques

Five different sample drying methods were used: freeze drying, air drying overnight at room temperature (23°C), oven drying for 2.5 hr at 60°C, oven drying for 1 hr at 105°C, and (for two samples) oven drying for 1 hr at 150°C. These methods are fairly self explanatory, with further details given by Cragin et al. (1983). Triplicate subsamples were dried separately for each homogenized sample.

Soil and sediment digestion

Two wet digestion procedures were evaluated: a mild digestion using HNO_3 at 70°C for 3 hr and a more vigorous technique using HNO_3 in a high-pressure Parr bomb at 130°C for 3 hr. For the first procedure, 1.5 g

(\pm 0.01 g) of soil or sediment was weighed into a 50-mL digestion tube and 15.0 mL of concentrated GFS (G. Frederick Smith) redistilled HNO_3 added. Samples were then heated to 75°C for 3 hr in either a water bath or block digester and swirled occasionally. After cooling and settling, 10.0 mL of supernatant was pipetted into a 60-mL polyethylene (CPE) bottle and the sample diluted to 50.0 mL with 18 megohm deionized water (QW) from a Millipore Milli-Q system ($\text{Hg} < 0.1 \text{ ng/L}$).

For the Parr bomb digestions, 1 to 2 g (\pm 0.001 g) of sample was placed in the Teflon cup of the bomb and 3.00 mL of GFS redistilled HNO_3 added. The bomb was then sealed and heated in an oven to 130°C for 3 hr. After cooling, samples were diluted to 50.0 mL with QW. Appropriate amounts (0.5 to 20 mL depending upon the amount of solid sample digested and its Hg content) of this solution were removed for analysis.

Duplicate or triplicate digestions were performed on all samples.

Sampling method

With the Jerome Model 301 Gold Film Mercury Detector (GFMD), Hg analyses can be performed directly on dry soil samples or on liquid digests and standards. For dry soil or sediment analysis, the bulk sample was first homogenized by shaking in a closed container and a 0.1- to 0.2-g subsample (containing 5-20 ng Hg) weighed into a Pyrex combustion vial. The vial was then heated on a hotplate to 300°C to drive off Hg^0 vapor and purged with Hg-free air for 1 min to carry the sample Hg to the instrument collector.

Liquid analyses followed the chemical reduction volatilization procedure of Hatch and Ott (1968). For 100-mL samples, the following optimum reagent volumes were found: 2 drops of 5% w/v KMnO_4 (Coleman), 1.35 mL of GFS concentrated redistilled HNO_3 , 2.0 mL of concentrated H_2SO_4 (J.T. Baker Low Hg Reagent Grade) and 2.0 mL of 10% w/v SnCl_2 in 0.5 N HCl (both J.T. Baker Reagent Grade). Reagents were added in the order listed, allowing a 2-min reaction time between each. Immediately after addition of SnCl_2 , the sample container was capped and Hg-free air bubbled through the solution for 2 minutes to entrain Hg^0 vapor and transport it to the collector coil of the Model 301 GFMD. Aliquots of soil and sediment digests were diluted to 100 mL with QW. For larger volume (e.g. 800-mL) standards used in assessing instrumental precision, proportionally greater reagent volumes and purge times were used.

Analysis technique

To minimize contamination at the low levels of Hg present in many of these samples, all labware (conventional polyethylene) was cleaned by the following procedure: (1) rinsing with distilled water to remove dust particles, (2) rinsing with electronic-grade (low heavy metal content) acetone to remove oils and mold-release agent, (3) rinsing again with distilled water, (4) leaching in 20% redistilled HNO_3 (GFS) distilled water for at least 12 hours and finally (5) rinsing with QW.

Of the many existing analytical techniques for quantitative determination of mercury, two were available in our laboratory: cold vapor atomic absorption (CVAA) (Hatch and Ott 1968), the most frequently used method, and a relatively new technique using thin gold films for mercury detection (GFMD) (McNerney et al. 1972). Both techniques detect elemental mercury (Hg^0) vapor in a gas (generally air) stream formed by the addition of suitable reducing agents (SnCl_2 or NaBH_4) to a liquid sample. We selected the gold film mercury technique for three reasons: (1) the instrumental sensitivity is better than that for CVAA; (2) unlike CVAA, the gold film mercury detector (GFMD) is insensitive to interference from water vapor and thus presented the possibility of analyzing wet samples directly by "dry combustion"; and (3) analysis is somewhat faster, permitting a greater sample throughput. Comparison of these two techniques (GFMD and CVAA) has shown excellent agreement for organic liquid and wastewater samples (Murphy 1979). With the exception of the comparison study of Murphy (1979), however, very little has appeared in the literature on the new GFMD method, which offered us the opportunity to evaluate precision and accuracy of this technique for low levels (ng/L) of Hg.

The GFMD method is based upon the fact that the resistance of a thin gold film increases significantly when elemental mercury is adsorbed upon or amalgamated with it. The heart of the Jerome Instrument Model 301 Gold Film Mercury Detector is a Wheatstone bridge with gold films forming two of the arms. Over the reference film passes filtered air and over the other film passes the sample stream containing any elemental mercury vapor (Hg^0) present in the sample. The resistance difference is converted into a voltage signal proportional to the absolute amount of mercury present. In the air stream just ahead of the films is a gold "collector coil" that quantitatively collects Hg^0 vapor as it is released from the sample. Timed

electrical heating of this coil releases Hg^0 vapor into the flowing air stream which transports it to the measurement film.

RESULTS AND DISCUSSION

In order to assess recovery and precision of sample drying techniques, it was first necessary to determine the precision of the analytical method and the recovery and precision of the sample digestion technique. We will thus initially address the final procedural step, instrumental variability, and subsequently examine sample digestion and drying.

Instrumental precision

For the analysis technique, we examined instrumental precision of the Jerome Model 301 Gold Film Mercury Detector by using acidified aqueous standards containing from 1 to 10 ng Hg in 100-mL or 800-mL aliquots (concentration range 1.25 to 100 ng Hg/L). Figure 1 shows that the absolute standard deviation of the analysis increases with the amount of mercury present in the sample. There is no significant difference in precision between 100-mL and 800-mL aliquots and thus precision depends

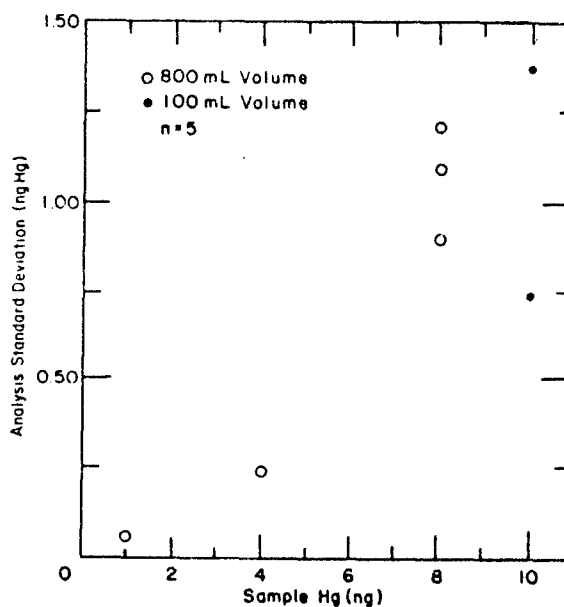


Figure 1. Absolute instrumental precision of gold film mercury detector for aqueous standards containing various amounts of mercury. Multiple points for the 8- and 10-ng samples are for multiple analyses on different days.

Table 1. Relative precision for analysis of Hg in sediment and soil samples by the dry combustion technique.

Sample	No. of replicates	Mean Hg(ng/g)	σ (ng)	RSD(%)
Arizona soil	11	99	11.0	11.1
Charlton silt	4	173	22.8	13.1
Windsor sand	4	58	3.4	5.8
NBS River sediment	4	735	90	12.3

upon the absolute amount of mercury present in the sample and not on its concentration in solution. Relative precision averaged 10.4% and did not show any clear trend with the amount of Hg present. Attempts to reduce the 10% RSD by varying instrumental parameters did not result in any appreciable improvement.

Since the above precision was for liquid standards, we next compared the precision of analysis for solid samples within the "dry combustion" technique. Here the sample was heated to 300°C in a glass ampule and Hg vapor was purged and collected directly on a gold film (the collector) in the instrument. This procedure has the advantage of requiring no digestion or reagents. Results, given in Table 1, show essentially the same precision as was obtained for the analysis of aqueous standards. Initially the dry combustion technique offered promise of being able to analyze samples directly without digestion and, although it worked well for soils and samples of low (<30%) moisture content, the Kewaunee sediment (120% moisture) and Louisiana army ammunition plant pond sediment (88% moisture) gave erratic results.

Instrumental accuracy

The accuracy of the GFMD was checked both with liquid samples of known Hg concentration from the U.S. Environmental Protection Agency (EPA) and with soil and sediment samples from the U.S. National Bureau of Standards, the National Research Council of Canada and Jerome Instrument Co. (the manufacturer of the GFMD instrument). Experimental concentrations (Table 2) agree very well with certified values within the standard deviations given. Results from the sediment samples also provide verification of the completeness of the digestion techniques (HNO₃ at 75°C) discussed below.

Table 2. Analysis of certified water and sediment samples.

Sample	Hg found	Certified value	Concentration units
EPA trace metals #1	380 \pm 45	400	ng/L
NBS Hg in water	1.04 \pm 0.11	1.10 \pm 0.06	μ g/L
NBS river sediment**	0.74 \pm 0.12	1.1 \pm 0.5	μ g/g*
NBS estuarine sediment**	62 \pm 5	63 \pm 12	ng/g*
Canadian marine sediment MESS**	170 \pm 10	171 \pm 14	ng/g*
Canadian marine sediment BCSS**	131 \pm 7	129 \pm 12	ng/g*
Arizona soil (Jerome Instrument Co.)**	98 \pm 8	100 to 150	ng/g*

*Values are on a dry weight basis.

**Sample digested in HNO₃ at 75°C for 3 hours.

Sample digestion

Mercury exists in the earth's crust mainly as the sulfide ore, cinnabar (HgS). The presence of Hg in soils and sediments is generally due to contamination from natural (volcanic and geothermal) or anthropogenic sources. Since Hg is not part of the silicate matrix of soils and sediments but is usually sorbed on particle surfaces or complexed with organic matter, a rigorous acid dissolution or sodium carbonate fusion is probably not necessary for complete Hg recovery. Consequently, we selected mild (concentrated HNO₃ at 75°C) and moderate (high pressure Parr bomb, concentrated HNO₃, 130°C) digestion methods for comparison. The Parr bomb is commonly used for solid sample digestions, and quantitative recoveries have been obtained for many other metals. The HNO₃ at 75°C technique was devised because it requires less capital expense and is simpler and faster for a large number of samples.

We digested eight soil and sediment samples (Table 3) using the above two soil techniques and the dry combustion procedure described previously. Some of the samples contained low amounts of moisture (Arizona soil, Windsor sand, Charlton silt) and two had been previously dried (NBS river sediment, NBS estuarine sediment) but the other sediment samples had high moisture contents. For a given sample, mercury concentrations agree, within the standard deviations listed, for all digestion techniques. The NBS estuarine sediment and LAAP pond sediment samples contained interferences (possibly salts or organic matter or high moisture) that produced

Table 3. Comparison of sample digestion techniques.

Sample	Digestion technique					
	Dry combustion		HNO ₃ , Water bath, 75°C		HNO ₃ , Parr bomb, 130°C	
	Hg(ng/g)*	RSD(%)	Hg(ng/g)*	RSD(%)	Hg(ng/g)*	RSD(%)
Arizona soil	99	11.1	98	8.2	97	3.3
NSS river sediment	735	12.3	760	5.7	732	8.9
NBS estuarine sediment	**	**	62	15.8	-	-
Charlton silt	173	13.1	163	8.2	-	-
Charlton silt†	1335	13.0	1349	5.0	1293	5.0
Windsor sand	58	5.8	62	15.8	-	-
LAAP pond sediment	**	**	1843	5.2	1892	11.2
Kewaunee sediment	48	10	48	5.3	44	2.0

*Dry weight

†Treated with wastewater

**Interference in analysis

erratic results when analyzed directly by dry combustion. The agreement of experimental values for the NBS samples with certified values (previous section) further suggests that these digestion techniques are also quantitative. Because of its speed and rapidity, the 75°C HNO₃ method was used to digest all subsequent samples used to compare sample drying techniques.

Sample drying

Four different samples, two soils and two sediments, were selected to evaluate the effects of drying on Hg recovery. Moisture contents of the samples ranged from 13.6 to 120% (Table 4). The values given in Table 4 are averages of moisture content for all drying techniques. Moisture contents determined by the separate drying techniques agreed to within 1.7% water (absolute deviation) for each of the four samples. This absolute variability is equivalent to 1.1 to 5.5% relative standard deviation, depending on sample moisture content.

Table 4. Moisture contents of soil and sediment samples used for drying.

Sample	Moisture content (%)	σ (%)
Charlton silt	30.1 \pm 0.8	2.7
Windsor sand	13.6 \pm 0.8	5.5
Kewaunee sediment	120.4 \pm 1.3	1.1
LAAP Pond sediment	88.3 \pm 1.7	1.9

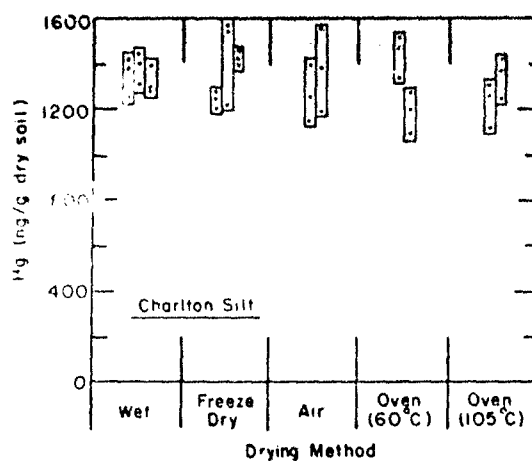


Figure 2. Mercury recoveries from Charlton silt for various drying techniques.

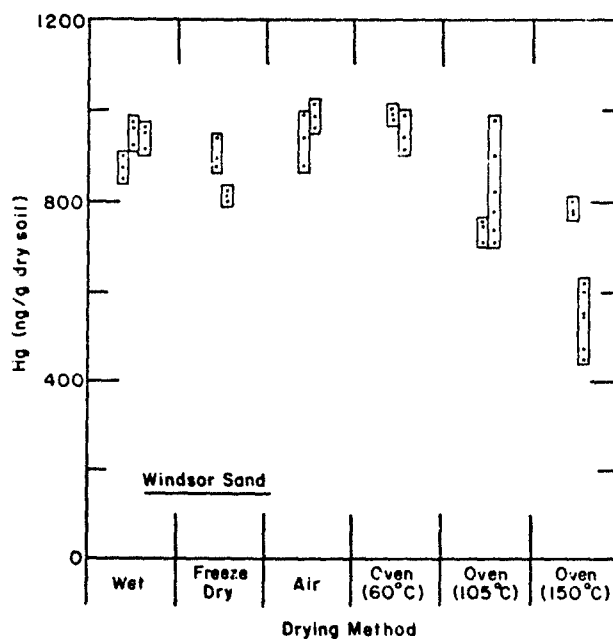


Figure 3. Mercury recoveries from Windsor sand for various drying techniques.

Table 5. Concentrations of Hg in wet and dried soil and sediment samples.

Charlton soil		Windsor sand*	
Drying method	Hg(ng/g dry weight)	Drying method	Hg(ng/g dry weight)
	#1 #2 #3		#1 #2 #3
Undried (wet)	1260 1310 1280 1380 1400 1290 1410 1440 1390	Undried (wet)	850 940 930 870 960 960 900 970 950
Freeze dry	1200 1540 1460 1270 1570 1390 1250 1220 1420	Freeze dry	880 820 940 800 920 810
Air	1260 1190 1150 1380 1390 1550	Air	880 920 940 1010 890 960
Oven 60°C	1340 1090 1470 1270 1520 1200	Oven 60°C	990 930 980 930 1000 910
Oven 105°C	1270 1370 1310 1250 1120 1420	Oven 105°C	750 980 710 710 750 900 820 820 740 740 780 780
		Oven 150°C	780 640 800 450 770 550 470 470 530 530

*This sample is from a different soil horizon than

Kewaunee Sediment

LAAP Pond Sediment

Drying method	Hg(ng/g dry weight)			Drying method	Hg(ng/g dry weight)		
	#1	#2	#3		#1	#2	#3
Undried (wet)	46.0	46.0	53.0	Undried (wet)	1760	1700	1770
	48.9	46.4	44.3		1910	1840	1820
	49.3	47.1	47.9		1980	1860	1740
Freeze dry	39.4	48.0	53.8	Freeze dry	2180	1840	
	46.5	46.1	50.8		2400	1720	
	45.8	45.2	46.1		1920	2200	
Air	59.8	57.6	56.4	Air	1840	1760	
	57.8	54.0	54.1		2400	1720	
	59.1	54.2	59.3		2180	2140	
Oven 60°C	57.3	63.4		Oven 60°C	1900	1680	
	55.3	59.0			2260	1840	
	59.5	47.9			2200	1920	
Oven 105°C	59.4	49.0		Oven 60°C	1760	2040	
	64.2	48.1			1980	1600	
	57.7	50.6			1640	2180	
				Oven 105°C	1820	1960	
					1840	2180	
					1800	1940	
				Oven 105°C	2060	1940	
					2140	1530	
					2340	2090	
				Oven 150°C		1860	
						1400	
						1530	
				Oven 150°C	720	1680	
					660	1460	
					600	1560	
					610	1700	
					740	1620	
					760	1680	

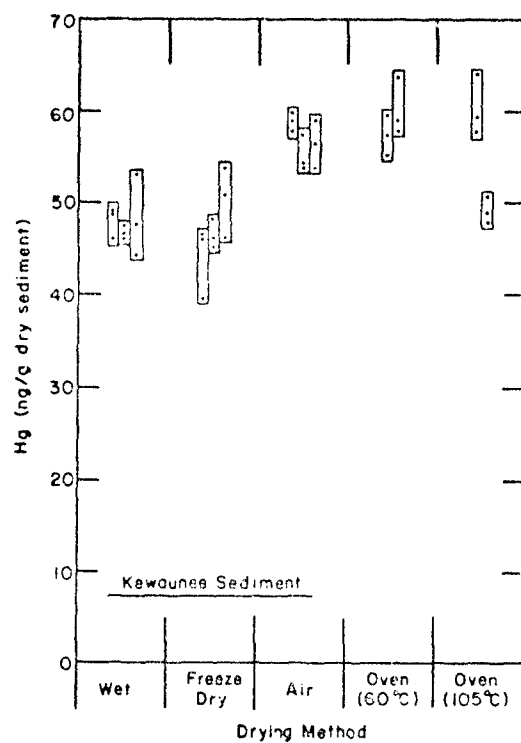


Figure 4. Mercury recoveries from Kewaunee sediment for various drying techniques.

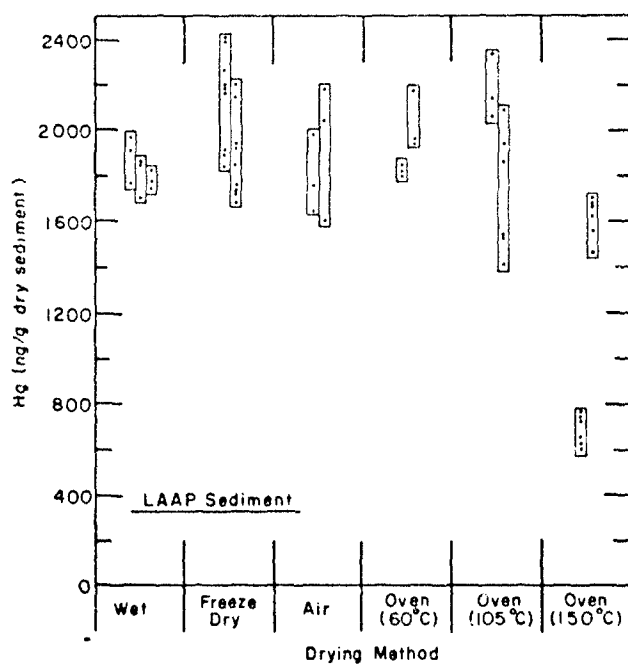


Figure 5. Mercury recoveries from LAAP sediment for various drying techniques.

Table 6. Mercury recoveries and results of analysis of variance for different drying techniques.

Sample	Drying method	Mean Hg recovery (ng/g dry weight)
Charlton silt	Undried	1349 ± 63 a*
	Freeze dry	1369 ± 140 a
	Air	1320 ± 140 a
	Oven 60°C	1313 ± 154 a
	Oven 105°C	1290 ± 96 a
Windsor sand	Undried	913 ± 47 bc
	Freeze dry	862 ± 60 bc
	Air	945 ± 52 b
	Oven 60°C	968 ± 36 b
	Oven 105°C	815 ± 122 c
	Oven 150°C	663 ± 141 d
Kewaunee sediment	Undried	47.7 ± 2.5 e
	Freeze dry	46.9 ± 4.0 e
	Air	56.9 ± 2.4 f
	Oven 60°C	57.1 ± 4.9 f
	Oven 105°C	54.8 ± 6.1 f
LAAP pond sediment	Undried	1843 ± 96 g
	Freeze dry	2005 ± 230 g
	Air	1867 ± 234 g
	Oven 60°C	1923 ± 142 g
	Oven 105°C	1947 ± 320 g
	Oven 150°C	1150 ± 520 h

*Letters indicate significance at the 95% confidence level. For each sample, recoveries with the same letter are not significantly different.

Mercury concentrations in these four samples are listed in Table 5 and shown more clearly in Figures 2-5 for each drying technique. In these figures each vertical bar represents one dried sample and the points within are values of Hg obtained from separate analyses of that particular subsample. These plots show that for each sample the variability between analyses of a given dried subsample is similar to the variability between different dried subsamples. Thus much, if not most, of the analytical variability can be attributed to the instrumental technique (GFMD) itself.

Average mercury recoveries and results of an analysis of variance are summarized in Table 6. All drying techniques resulted in statistically equivalent Hg recoveries for the Charlton silt. For Windsor sand, the wet, freeze-dried, air-dried and 60°C oven-dried samples gave Hg recoveries that

were not significantly different at the 95% level; Hg recovery from the 105°C oven-dried Windsor sand sample was significantly lower than from the air-dried and 60°C oven-dried samples but was not significantly different from the wet and freeze-dried samples; this may be due to Hg recoveries of the air-dried and 60°C oven-dried samples being somewhat (although not significantly) higher than Hg recovery from the wet sample. The lowest average Hg recovery for Windsor sand was obtained for the 150°C oven-dried sample which was significantly lower than all other drying types.

For the Kewaunee sediment, wet and freeze-dried Hg recoveries were significantly different from the air-dried, 60°C oven-dried and 105°C oven-dried samples. A surprising aspect of this result, though, is that the latter three techniques gave higher Hg recoveries than the wet and freeze-dried methods. This may be due to a spuriously low wet recovery and loss during freeze drying. During freeze drying, the vacuum imposed upon the sample could have resulted in volatilization loss of Hg that is still "liquid" (in contrast to water) at the freezing temperature employed (approximately -15°C) and can volatilize more readily. This process would be more noticeable at low Hg concentrations such as those present in the Kewaunee samples. However, although this explanation seems plausible, we have no experimental evidence to verify it.

Finally, for the LAAP pond sediment, Hg recoveries were not statistically different except for 150°C oven drying which was significantly lower. The large difference in Hg recovery from the two different 150°C dried samples (Fig. 5) may be due to variation in volatilization losses at the higher drying temperature.

SUMMARY AND CONCLUSIONS

Amalgamation on thin gold films (Jerome Instrument Model 301 Hg detector) is an accurate method for determination of mercury in soils and sediments. Relative analytical precision of this technique is about 10% over the range of 40 ng to 2 µg Hg/g. While some soils can be analyzed directly without digestion, the high water content and more complex matrix of sediments require that such samples first be digested. Comparison with NBS certified standards showed that digestion in HNO₃ at 75°C results in quantitative recovery of mercury from soils and sediments.

Mercury loss from soils and sediments associated with various drying techniques depends upon sample type and possibly upon sample Hg concentra-

tion. In no case did Hg recovery for freeze-dried samples differ significantly from that of undried (wet) samples, but both wet and freeze-dried Kewaunee sediment samples had significantly lower Hg recoveries than air- and 60°C oven-dried Kewaunee samples. This could have been caused by Hg losses from the wet and freeze-dried samples or by contamination of the air- and oven-dried samples but the exact cause has not been resolved. Oven drying at 150°C resulted in significantly lower Hg recovery for both soil and sediment samples. Air drying at room temperature and oven drying at 60°C resulted in quantitative Hg recoveries for the Charlton and Windsor soils and Louisiana AAP pond sediment. Overall, freeze-dried, air-dried, 60°C oven-dried and wet Hg recoveries agreed within 20%. Thus, for Hg determinations in soils and sediments, any one of these three comparable methods are recommended.

The significance of Hg recoveries is influenced by the precision ($\pm 10\%$) of the analytical method. Improvement of analysis precision might result in more restrictive recommendations. Although the GFMD technique is more sensitive for Hg, cold vapor atomic absorption spectrometry (CVAA) generally possesses better precision. In the future, analysis precision might be improved without a loss of sensitivity by combining the collector cycle of the GFMD with CVAA detection.

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